production in the blood stream, either directly via an effect on mononuclear cells or indirectly via an effect on the alternative complement pathway. Conversely, the majority of the mediators that are potentially elicited in the blood, such as C3a and IL-1, may be simultaneously eliminated during high flux therapies by an adsorptive or transmembrane mechanism, as discussed above. Other investigations have confirmed that adsorption is also important in the removal of other inflammatory mediators, such as Factor D and cytokines.

Summary

Dialysers used in contemporary HD are equipped with a wide variety of membranes and within both the cellulosic and synthetic classes, water and solute flux properties vary widely. For small and middle-sized solutes, abundant clinical data point to the importance of membrane thickness in diffusive mass transfer. The removal of low molecular mass proteins may occur largely by adsorption for some high flux membranes, particularly those of hydrophobic synthetic composition. Because many of the mediators of inflammation in dialysis patients fall in this low molecular mass protein category, the biocompatibility of a particular membrane must be interpreted in conjunction with its permeability properties.

See Colour Plate 47.

See also: **II/Membrane Separations:** Membrane Bioseparations. **III/Membrane Preparation:** Hollow Fibre Membranes; Interfacial Composite Membranes.

Further Reading

Anderstam B, Mamoun A, Sodersten P and Bergstrom J (1996) Middle-sized molecule fractions isolated from uraemic ultrafiltrate and normal urine inhibit ingestive behavior in the rat. *Journal of the American Society of Nephrology* 7: 2453–2460.

Cheung AK, Parker C, Wilcox L and Janatova J (1990) Activation of complement by haemodialysis membranes: polyacrylonitrile binds more C3a than cuprophan. *Kidney International* 37: 1055–1059.

Clark WR, Macias WL, Molitoris A and Wang NHL (1995) Plasma protein adsorption to highly permeable haemodialysis membranes. *Kidney International* 48: 481–488.

Clark WR, Hamburger RJ and Lysaght MJ (in press) The effect of membrane composition and structure on solute removal and biocompatibility in haemodialysis. *Kidney International*.

Colton C, Henderson L, Ford C and Lysaght M (1975) Kinetics of hemodiafiltration. I. *In vitro* transport characteristics of a hollow fiber blood ultrafilter. *Journal of Laboratory and Clinical Medicine* 85: 355–371.

Deppisch R, Gohl H and Smeby L (1998) Microdomain structure of polymeric surfaces – potential for improving blood treatment procedures. *Nephrology, Dialysis and Transplantation* 13: 1354–1359.

Henderson L (1996) In Jacobs C, Kjellstrand C, Koch K and Winchester J (eds) *Biophysics of Ultrafiltration and Hemofiltration*, 4th edition, pp. 114–145. Dordrecht: Kluwer Academic Publishers.

Henderson L, Colton C and Ford C (1975) Kinetics of hemodiafiltration. II. Clinical characterization of a new blood cleansing modality. *Journal of Laboratory and Clinical Medicine* 85: 372–391.

Jindal KK, McDougall J, Woods B, Nowakowski L and Goldstein MB (1989) A study of the basic principles determining the performance of several high-flux dialyzers. *American Journal of Kidney Disease* 14: 507–511.

Ledebo I (1998) Principles and practice of hemofiltration and hemodiafiltration. *Artificial Organs* 22: 20–25.

Leypoldt JK, Cheung A, Agodoa L, Daugirdas J, Greene T and Keshaviah P (1997) Hemodialyzer mass transfer-area coefficients for urea increase at high dialysate flow rates. *Kidney International* 51: 2013–2017.

Lipps B, Stewart R, Perkins H, Holmes G, McLain E, Rolfs M and Oja P (1967) The hollow fibre artificial kidney. *Transactions of the American Society of Artificial Internal Organs* 13: 200–207.

Lonneman G (1993) Dialysate bacteriological quality and the permeability of dialyzer membranes to pyrogens. *Kidney International* (Suppl. 41) S195–S200.

Lysaght MJ (1988) Haemodialysis membranes in transition. *Contributions to Nephrology* 61: 1–17.

Vanholder R and DeSmet R (1999) Pathophysiologic effects of uremic retention solutes. *Journal of the American Soceity of Nephrology* 10: 1815–1823.

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Diffusion Dialysis

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Introduction

Diffusion dialysis is a separation process in which an ion exchange membrane separates a source solution and a receiving solution, usually water. Anion exchange membranes are notoriously permeable to acids, and diffusion dialysis exploits this property to separate acids from salts. A common application of diffusion dialysis is recovery of acids from waste metal pickling solutions, the strong acid solutions that are used to remove oxide coatings from metal parts before they are painted, galvanized or

electroplated. Cation exchange membranes are permeable to bases, and this is utilized to recover NaOH from aluminium etching solutions.

Diffusion dialysis of acids through anion exchange membranes was reported as early as 1964, and was installed on an industrial scale by 1980. There have been many laboratory studies on membrane properties and transport of acid through such membranes. Therefore, the discussions that follow concerning the theory and practice of diffusion dialysis will focus primarily on acid transport through anion exchange membranes. Base dialysis is relatively new, and there is not a large body of knowledge about the mechanism of transport, design criteria and performance of that process. Until such information becomes available, it is reasonable to assume that the theory and practice of base dialysis parallels that of acid dialysis.

Since ion exchange membranes have an ionically charged polymeric structure, their discrimination between solutes is based on ionic charge. Anion exchange membranes are easily permeated by anions, but cations are rejected, because the positive ionic change of the membrane matrix repels the cations. Unlike other cations, hydrogen ions are an integral part of the water that pervades the membrane, and hydrogen ions seem to permeate by a different mechanism that avoids the rejection of the charged polymer structure. Anion exchange membranes transport acids while rejecting salts.

Figure 1 illustrates diffusion dialysis for recovery of HNO_3 from a solution also containing $Fe(NO_3)_2$. The anion exchange membrane is quite permeable to the NO_3^- ions, but an equivalent amount of cations must also pass through the membrane to maintain electroneutrality. Because of their double positive charge, the Fe^{2+} ions are strongly rejected by the membrane, but the protons are transported rather easily. Thus, a useful separation of acid and salt is achieved.

Background and Theory

Transport in diffusion dialysis is described by Fick's law:

$$\text{Flux} = -U\,\Delta C \qquad [1]$$

where ΔC is the concentration difference of the diffusing solute (the driving force for diffusion) and U is a mass transfer coefficient, expressed in units of length time^{-1}. Since the concentrations can be measured only in the bulk solutions, the measured value of ΔC is the driving force for diffusion through the membrane and the solution boundary layers next to the membrane. Therefore, an overall mass transfer coefficient U_o is needed to describe the observed flux. The reciprocal of the mass transfer coefficient is the diffusional resistance, and the diffusional resistances of the membrane and the adjacent liquid boundary layers are additive.

$$1/U_o = 1/U_m + 1/U_l \qquad [2]$$

Values of U for a particular solute through a particular membrane are conveniently measured in a stirred cell with the membrane separating the source solution from the receiving solution, usually pure water. With sufficient stirring the resistance of the liquid can be minimized so that the measured value of U is essentially U_m. Acids permeate some anion exchange

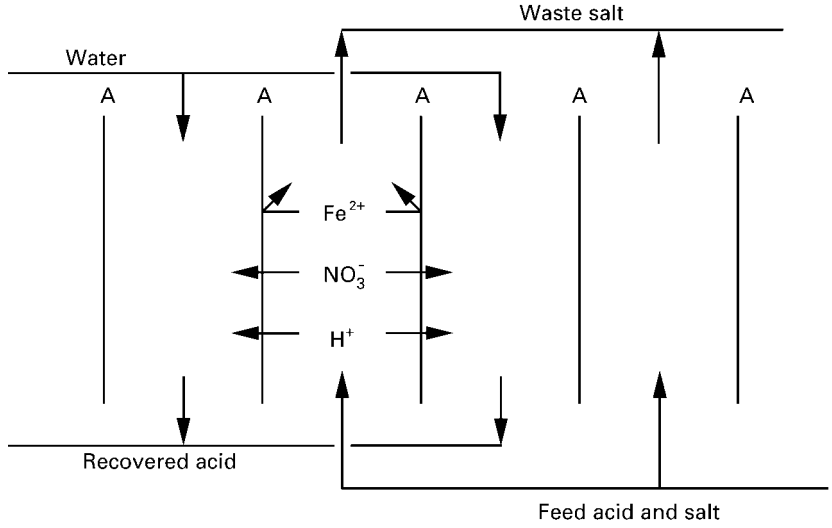

Figure 1 Diffusion dialysis to recover HNO_3 from pickling solution.

membranes rapidly, with U values of about 10^{-4} to 10^{-3} cm s^{-1} while salts have U values of about 10^{-6} cm s^{-1}. Therefore, there is sufficient difference in the diffusion rates to achieve useful separations of acids from salts by diffusion dialysis.

Since solution velocities in commercial dialysers are slow, U_l could be a significant part of U_o. A rough idea of the resistance in the boundary layer can be estimated by examining the elements of the equation for diffusive flux through a film of liquid:

$$\text{Flux} = -D\,\Delta C/z \qquad [3]$$

where D is the diffusivity of the solute through the solvent, typically about 10^{-5} cm^2 s^{-1}, and z is the thickness of the film of liquid through which diffusion occurs. Spacing between membranes in a commercial dialysis apparatus is somewhat less than 0.1 cm, so liquid film thickness z would probably be about 0.01 cm. Then $D/z = 10^{-3}$ cm s^{-1}, which is a U value for the liquid film of the same order of magnitude as the typical U values for dialysis membranes.

Consequently, both the membrane and the liquid films in contact with it are likely to contribute to the resistance to diffusion in a real dialysis application, even at rather high solution velocities.

Transport of solvent through dialysis membranes can be great enough to influence diffusion dialysis performance. Osmotic forces provide a driving force to transport solvent from the dilute solution to the concentrated solution. However, the diffusing solute can drag along solvent, both in the solvation shells of the ions and by convection, in the direction opposite to that of normal osmosis. Further, osmotic pressures are caused by the concentration difference of nondiffusing solutes across the membrane, the values of which can be difficult to determine. Consequently, even the direction of solvent transport can be difficult to predict in certain circumstances, and prediction of the rate of solvent transport is quite difficult.

Mathematical analysis of dialysis is rather simple if the assumptions are made that the overall value of U is independent of C and that solvent transport is negligible. There are two typical cases that are usually encountered with dialysis in general or with diffusion dialysis.

Case 1 is an experiment done in an apparatus used to measure dialysis coefficients, i.e. U values. A sample of the membrane is placed between two chambers of equal volume in a stirred cell, with a surface area A exposed to both solutions. The source solution fills one chamber, and an equal volume V of pure water, the receiving solution, fills the other chamber. Because the volumes of the two solutions are equal, the concentration of the diffusing solute decreases in the source solution at the same rate as it rises in the receiving solution on the other side of the membrane. The rate of concentration change, dC/dt, is related to the flux, volume and area of the membrane by the equations below. On the side containing the receiving solution:

$$dC/dt = \text{flux} \times A/V \qquad [4]$$

and on the side containing the source solution:

$$dC/dt = -\text{flux} \times A/V \qquad [5]$$

To integrate this equation, an expression is needed for flux in terms of concentrations on one side of the membrane. The appropriate expression can be obtained by material balance. Let C_s represent the concentration of the diffusing solute on the side with the source solution. Then the concentration of the diffusing solute in the receiving solution would be $C_r = C_0 - C_s$, where C_0 is the initial concentration of the source solution. Now an equation for solute flux can be written as follows:

$$\text{Flux} = -U \times \Delta C = -U \times [C_s - (C_0 - C_s)]$$

$$= -U \times (2C_s - C_0) \qquad [6]$$

The differential equation can be integrated to yield:

$$C_s = C_0(1 + e^{-2tUA/V})/2 \qquad [7]$$

on the side of the source solution and:

$$C_r = C_0(1 - e^{-2tUA/V})/2 \qquad [8]$$

on the side of the receiving solution.

The experiment described in case 1 is a useful technique for measuring values of U for a membrane. Sufficient stirring can reduce solution film resistance to negligible levels, and even volume changes are insignificant in short experiments. Volume changes and analytical inaccuracy can cause substantial errors if source solution concentrations are used in this determination, so determination of the U value should be based on the measured concentrations in the receiving solution.

Although the apparatus described in case 1 is useful for determining membrane properties, it is of limited commercial value as a separation process because no more than half of the diffusing solute can be removed when equal volumes are used on both sides of the membrane. A high degree of removal would require a volume of the receiving stream much larger than that of the feed, but that has limited commercial

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appeal. A commercially useful separation can be achieved with countercurrent flow of the solutions through the dialyser.

Case 2 is an example of countercurrent flow of the solutions on opposite sides of the membrane. The system operates at steady state so that concentrations do not change with time, but they do change with position along the flow path of the solutions. To simplify the equations it will be assumed that there is no solvent transport through the membrane and that the source and receiving solutions have the same flow rate, F. When pure water is used for the receiving stream, the material balance is simply:

$$C_f = C_d + C_r \quad [9]$$

where the subscripts represent the feed, depleted and recovered streams respectively. The amount of solute transferred across the membrane is equal to the amount of solute appearing in the recovered stream:

$$UA\,\Delta C = FC_r \quad [10]$$

Because the flow rates are equal, the concentration change within a solution compartment is linear with respect to distance along the flow path, so the concentration difference across the membrane is equal to the arithmetic mean concentration difference:

$$\Delta C = (C_f + C_d - C_r)/2 \quad [11]$$

Combining this with the material balance equation yields:

$$\Delta C = C_f - C_r \quad [12]$$

which can be combined with the transfer equation:

$$UA(C_f - C_r) = FC_r \quad [13]$$

and rearranged to show the fraction of solute recovered:

$$C_r/C_f = U/(U + F/A) \quad [14]$$

In practice, the values for U are often expressed in the same units as the flow rate per unit area of membrane, L h^{-1} m^{-2}. For the diffusion of HCl from pickle liquor through Neosepta AFN anion exchange membrane, reported values of U are 8.6 L h^{-1} m^{-2} for HCl and 0.17 L h^{-1} m^{-2} for Fe, and a typical value for F/A might be 1 L h^{-1} m^{-2}. With these values the HCl recovery would be $8.6/(8.6 + 1) = 0.9$, and the Fe leakage would be $0.17/(0.17 + 1) = 0.15$. Thus, 90% of the HCl is recovered, and 15% of the Fe appears in the recovered acid. Leakage of Fe could be reduced to 8% by doubling the flow rates, but HCl recovery would drop to 81%.

The simplified equation developed above for countercurrent dialysis is only applicable when flow rates of both streams in the dialyser are equal. For those more general situations with unequal flow rates, the log-mean concentration difference would be used as the driving force in Fick's law.

Deviations from Simple Modelling

Osmotic forces play a key role in the water balance, and water transport through the membrane can invalidate the simple mathematical models described above. The following discussion is based on the recovery of acid from a steel pickling solution, which is a significant industrial application of diffusion dialysis. In the recovery of acid from a mixture with a metal salt the major driving force for osmosis is the difference in concentration of salt across the membrane. The osmotic flow of water can cause the volume of the receiving stream to decrease as much as 20% as it passes through a typical industrial dialyser. Therefore, a good mathematical model of diffusion dialysis should account for water transport through the membrane.

The presence of salt in the source solution can substantially affect the concentration of acid in the recovered stream. In diffusion dialysis of metal pickle liquors the source solution has two important components – the free acid that can diffuse through the anion exchange membrane rather easily and the metal salt that is rejected by the membrane because of repulsion of the metal cations by the fixed positive charge on the membrane matrix. There are numerous reports of countercurrent diffusion dialysis in which the acid concentration in the recovered stream is higher than the free acid concentration in the feed. Some writers have attempted to explain these observations in terms of osmotic removal of water from the receiving stream, but it seems more plausible that a concentration difference of the common anion produces a driving force for transport of protons through the membrane. That driving force is the Donnan potential (discussed in 'Membrane Separations: Donnan Dialysis') generated by the difference between the activity of anions in the two solutions. That potential difference provides a driving force for proton transport in addition to the driving force provided by the difference in concentration of the free acid.

Fick's law describes acid flux due to simple diffusion as the product of the driving force ΔC_A and the mass transfer coefficient for diffusion, U_A. A similar expression can be used to describe the acid

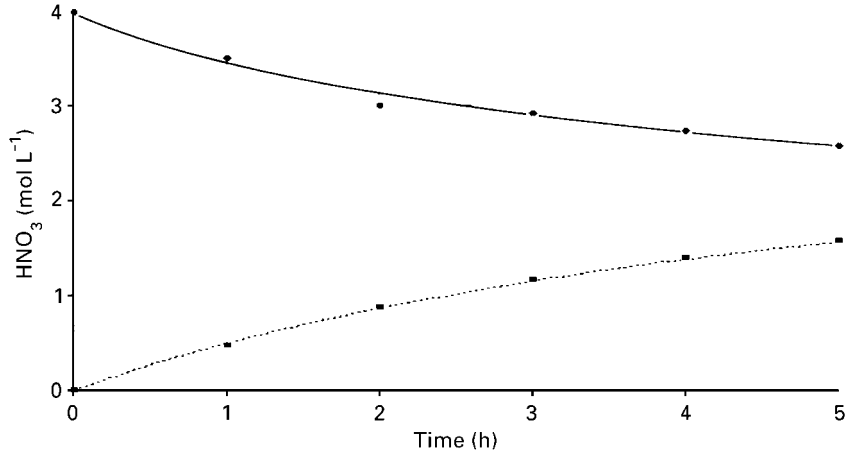

Figure 2 Diffusion dialysis of pure 4 mol L^{-1} HNO_3 feed stream (continuous line) with a pure water-receiving stream (dotted line).

transport due to the concentration difference of the salt with a common anion, with ΔC_S as the driving force and U_S as the mass transfer coefficient. The total acid flux can be expressed as the sum of the flux due to individual driving forces as follows:

$$\text{Total acid flux} = U_A \Delta C_A + U_S \Delta C_S \qquad [15]$$

This empirical equation was tested with published data by Edwards, who measured HNO_3 concentrations on both sides of a Tokuyama AFN membrane in a stirred cell. Graphs of data for three different starting compositions are shown in **Figures 2–4**. In each graph the data at the top connected by the continuous line show the reduction in concentration as acid diffuses from the source stream, and the data at the bottom show the increase in acid in the receiving stream. Figure 2 shows simple diffusion of HNO_3, which is well described by the dotted line that was calculated by Fick's law with $U_A = 12.8$ L h^{-1} m^{-2}. But when $NaNO_3$ was added to the source solution, Fick's law with $U_A = 12.8$ L h^{-1} m^{-2} (shown in Figure 3 by the dotted line) predicts a much slower appearance of acid than the data indicated. The equation for total acid flux with values of $U_A = 12.8$ L h^{-1} m^{-2} and $U_S = 0.45$ L h^{-1} m^{-2} shown by the dashed line gave a good correlation of the data. It is interesting to note in Figure 3 that the influence of the excess nitrate forced so much HNO_3 out of the source stream that its concentration fell below that in the receiving stream. The situation was reversed when NH_4NO_3 was placed in the receiving solution.

Figure 4 shows that the total acid flux equation with values of $U_A = 12.8$ L h^{-1} m^{-2} and $U_S =$

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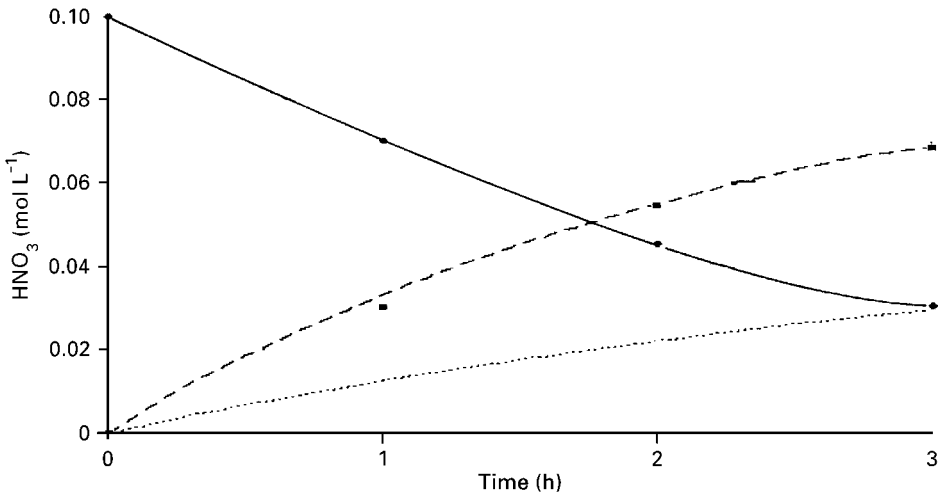

Figure 3 Diffusion dialysis of 0.1 mol L^{-1} HNO_3 and 5 mol L^{-1} $NaNO_3$ feed stream (continuous line) with a pure water-receiving stream (dashed and dotted lines). Lines calculated as described in the text.

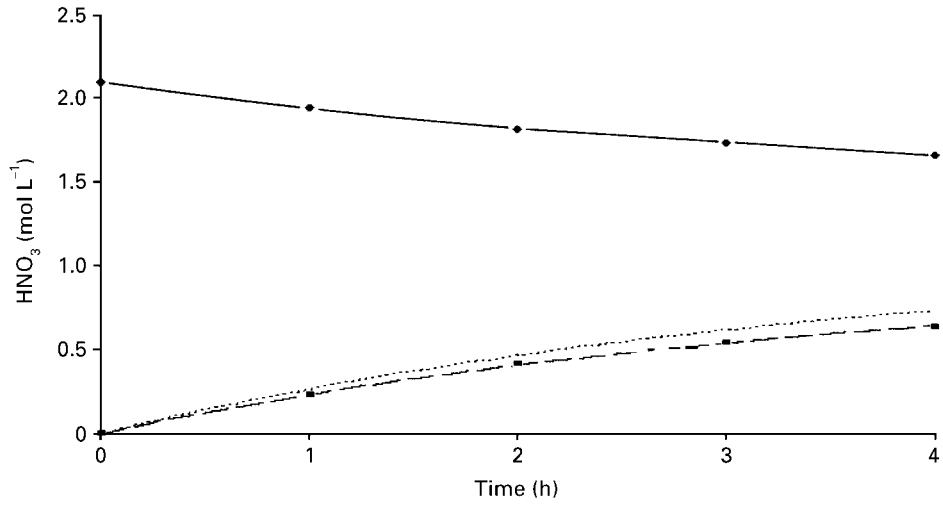

Figure 4 Diffusion dialysis of a 2.1 mol L^{-1} HNO_3 feed stream (continuous line) against a 4 mol L^{-1} NH_4NO_3-receiving solution (dashed and dotted lines).

0.45 L h^{-1} m^{-2} again described the data better than Fick's law and correctly showed that the appearance of acid in the receiving solution was retarded by the presence of nitrate in that solution. It should be emphasized that the total acid flux equation is empirical, but it does seem to be a useful way of accounting for the effects of salts on acid flux and would thus be useful for mathematical modelling of diffusion dialysis of acids.

Competing Processes

Diffusion dialysis, like most other membrane processes, must compete with other processes that can achieve the desired separation. Lime neutralization, sorption on ion exchange resins and bipolar membranes are competing processes for the treatment of waste acids from metal pickling. When disposal and replacement acid costs are low, lime neutralization is the most economical alternative. When the recovered acid can be used in a diluted form, sorption on ion exchange resins is attractive. When it is necessary to minimize discharge, bipolar membranes, though expensive, can be the preferred process. Diffusion dialysis offers the important advantages of very low operating costs and long membrane life that can exceed 5 years if clean, nonfouling feeds are used. Therefore, if diffusion dialysis can achieve the desired separation and if capital costs are tolerable, diffusion dialysis can be the process of choice for recovering waste acids.

Membranes for Diffusion Dialysis

Modern membranes for acid dialysis are made of anion exchange polymers which have an affinity for acids and reject cations other than protons. The anion exchange membranes that are most permeable to acids seem to be those with a very high water content. The water content is important because the high electromobility of protons through water is attributable to a transfer mechanism that is not available to other cations. A proton can transfer from a hydronium ion to an adjacent water molecule by a mechanism which was first suggested by Grotthus in 1806.

The major suppliers of diffusion dialysis membranes and devices are Asahi Glass, who make Selemion DMV, and Tokuyama Corporation who make Neosepta® AFN and AFX membranes. Since the membrane devices for diffusion dialysis are similar to those used in electrodialysis, any supplier of electrodialysis equipment is capable of supplying diffusion dialysis equipment as well. The supplier with the largest number of installations in the USA is Pure Cycle Environmental Technologies in Palmer, Massachusetts, and the largest supplier in Europe is Eurodia in Paris, France.

Membranes for base dialysis were parchmentized paper when the process was first developed in the 1930s. The early membranes had little selectivity between caustic and salts, but they effectively retained hemicellulose from rayon and viscose processes. Modern membranes for base dialysis are made of cation exchange polymer that rejects anions other than hydroxyl, presumably because of the Grotthus mechanism of hydroxyl transport. The typical cation exchange membrane made for electrodialysis has low flux for base diffusion, but Tokuyama Corporation has made a special cation exchange membrane, Neosepta® CMX-SB, with acceptably high flux.

Design of Processes and Equipment

Industrial diffusion dialysis usually operates with countercurrent flow of the solutions on opposite sides of the membrane. Countercurrent flow produces the maximum concentration difference over the entire length of the membrane and allows recovery of a substantial portion of the most highly diffusive solute while minimizing the transport of the less diffusive solutes. Since fluxes in diffusion dialysis are relatively low compared to other membrane processes, the solution velocity across the membrane surface must also be slow in order to have enough residence time for adequate removal of the solute. Typical solution velocities in diffusion dialysis are about 1 cm min^{-1}. Convective effects due to density changes in the solutions can be important with such low velocities.

Dialysers for industrial applications must be robust, cleanable, efficient and economical. Industrial diffusion dialysers usually have flat sheet membranes with some type of spacer to keep the membranes apart and to form solution compartments. The membrane arrangement (without showing the spacers) and the directions of solution flows in a typical diffusion dialyser are shown in Figure 1. A single dialyser can contain hundreds of identical, vertically oriented membranes. Membranes and spacers have holes that are aligned to form manifolds, and each spacer has entry ports that connect the solution compartment to the appropriate manifold. This manifolding, which is also typical in electrodialysis, distributes the solution equally to the parallel compartments. The feed solution usually enters the bottom of the dialyser and the solvent usually enters at the top, as shown in Figure 1.

Solutions flowing through the industrial diffusion dialyser should be free of particulate matter, because the solution velocities are too slow to sweep out particles. The dialyser can be expected to perform maintenance-free for several years if the feed solution is clean and no precipitation occurs within the dialyser. A single filter on each supply line should suffice if the feed solution is inherently clean. However, primary and secondary filtration is recommended if particles are expected to be present in the feed because of the possibility of contamination during the cleaning or replacement of primary filter elements.

The low solution velocities that characterize diffusion dialysis cause extremely low pressure drops through dialysers, usually just a few kPa. Many dialysers can be fed in parallel from a single header tank positioned just above the dialysers. The solutions exiting the dialysers also enter a header tank with adjustable overflow levels. The header tanks should have covers and filtered vents to avoid the entrance of dust. Transparent tanks or sight glasses positioned close together allow the operator to monitor visually the pressure drop through the dialyser. Density differences of the solutions should be considered in determining the actual pressure head.

In metal finishing plants the dialysis process is normally set up to run continuously to treat a small stream of the metal-laden acid in the pickling tank and return the recovered acid to the tank. This allows the dialysis to run as a steady-state process. The waste stream, which typically contains 10% of the acid and 90% of the metals from the feed, is usually neutralized to precipitate the metal as hydroxides for disposal or recovery.

It is important that the solution flow is uniformly distributed to all solution compartments that are fed in parallel. Density changes caused by solute transfer across the membranes are utilized to achieve uniform flow distribution. The feed solution, which has the highest density, enters the bottom of the dialyser and decreases in density as acid is removed. Osmotic water transport into this concentrated solution also contributes to the decrease in density. The receiving solution increases in density as it flows downward. The uniform gradation in density allows the solutions to approach plug-flow conditions in each solution compartment.

Entrapped gas can cause flow disruptions in the receiving solution compartments of acid dialysers. Water entering the top of the receiving solution compartments contains some dissolved gases (O_2, N_2, CO_2) that can form bubbles in the downward-flowing solution. Even if the water is not initially supersaturated with dissolved gases, the addition of solute diffusing across the membrane can lead to supersaturation within the receiving stream. The slow downward flow of solution is not sufficient to force the bubbles out the bottom of the dialyser, but it could hinder their rise in the compartments, Bubbles eventually reach such a large size that buoyancy forces exceed the forces of surface tension. Then the large bubbles rise and collect in the top of the compartment and eventually in the entry ports where they block off the flow of water into some of the receiving solution compartment. As more compartments become blocked, the solution velocity in the remaining compartments increases. But that increase in flow rate means that the residence time in those open compartments is shorter, so the performance of the dialyser deteriorates.

Removal of the dissolved gases from the water before it enters the dialyser is beneficial. Gases can be removed by heating the water in an open or vented tank, by application of a vacuum or by passing the

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water through a nonwetting microfiltration device with a vacuum applied to the opposite side of the microporous membrane. Another remedy is periodically to reverse the flow of the receiving stream and force the bubbles out of the top of the dialyser into a vent tank. Flow reversal can be accomplished easily with a centrifugal pump situated in the line of the receiving solution at the entrance or exit to the dialyser. The header tanks must have sufficient surge capacity to accommodate the volume of the flow reversal. Flow reversal for a few seconds is sufficient – just long enough to displace any gas that has accumulated in the top of the receiving compartments and entry ports. These two remedies are often used together.

The heat of dilution of the acid can also cause problems of overheating in diffusion dialysis. Because the dialyser acts like a countercurrent heat exchanger, the heat released in the dialyser tends to become trapped inside. When the concentration of acid in the feed is high, the peak temperature, which occurs about halfway through the flow path, can be high enough to damage the membrane.

Limitations of Diffusion Dialysis

A necessary condition of dialysis is that the solute concentration in the recovery stream must be lower than in the feed stream in order to provide a driving force for diffusion. This is not a real limitation in applications where the diffusing solute is a waste that can be easily discarded. But this condition can be a limitation when the diffusing solute is the desired product, because the product is often recovered at a low concentration. Fortunately, the acid from steel pickling solution can be recycled to the pickling bath at the concentration at which it was recovered. Another limitation is that the nondiffusing solutes are left in the original solution in a slightly diluted state, which means that the waste volume can be considerable.

The selectivity of diffusion dialysis membranes for rejecting metal ions is influenced by the ionic charge on the metal ion. Metal ions with multiple positive charge are rejected more efficiently than ions with a single charge. However, zinc and some other metal ions form complexes with the anions of the acid. In HCl solutions, zinc forms $ZnCl_3^-$ and $ZnCl_4^{2-}$ complexes that behave as anions in the anion exchange membrane. These complex ions do not diffuse through the membrane as readily as Cl^- ions do, but they diffuse much faster than Zn^{2+} ions. However, zinc does not form a complex in H_2SO_4 solution, so zinc is rejected quite well in the sulfate system.

All of the halogens form complexes with some metals. Chloride complexes of Cu, Ga, Fe (ferric forms a much stronger chloride complex than ferrous), V and Zn have been reported. The existence of a chloride complex does not necessarily mean that HCl cannot be recovered from the metal salt by diffusion dialysis. Since the chloride complexes are rather bulky, they do not pass through the anion exchange membranes as easily as chloride ions do.

Applications

The first important industrial application for dialysis seems to have been for recovery of caustic from viscose, hemicellulose, wood-pulping solutions and textile-processing solutions. In the 1930s there were many patents describing dialysers that utilized diaphragms of parchmentized paper and regenerated cellulose. Publications of that era described dialysis as a method for separating crystalloids (substances that form true solutions and are capable of being crystallized) from colloids (small particles in suspension).

By far the most important application for dialysis was begun during the 1940s when Dr. Willem Kolff discovered that treatment of blood by dialysis removed urea and other metabolic wastes, and he proceeded to develop the artificial kidney. The artificial kidney and other conventional dialysis processes are described in detail in 'Membrane Separations: Dialysis in Medical Separations'.

Conclusion

Diffusion dialysis utilizes membranes that contain ion exchange groups, and those were not available until the 1950s. Diffusion dialysis plants have been recovering and recycling acids in Japan since 1980, and many are being installed in the USA, particularly in metal-finishing facilities. Acids that have been recovered include HCl, HF, HNO_3, H_2SO_4 and methanesulfonic. The recovered acid is sufficiently concentrated to be returned to the pickling tank, and the acid-free solution of metal salts requires considerably less base to precipitate the metal hydroxides. Recovery of mixed HF and HNO_3 from the pickling of stainless steel is important because these cids are expensive and cause severe pollution problems if they are discarded. Diffusion dialysis has been applied to the recovery of H_2SO_4 from aluminium anodizing baths where the trivalent aluminium cation is well rejected by the anion exchange membrane.

Base dialysis membranes have been used commercially for the recovery of NaOH from the waste

generated by the chemical milling of aluminium aircraft parts. Chemical milling is used to remove metal from aluminium parts, such as curved sections of wing or fuselage that are difficult to machine with mechanical devices. The part is dip-coated with a film of rubber, and then a selected portion of the rubber is stripped away to expose the metal surface. Then the part is immersed in boiling NaOH that rapidly and uniformly dissolves the metal from the exposed surface. The dissolved aluminium accumulates in the etch tank as $NaAlO_2$, which must be discarded eventually. When the NaOH is removed from the solution by dialysis, the $NaAlO_2$ hydrolyses to $Al(OH)_3$ and NaOH. The $Al(OH)_3$ is recovered by filtration and sold as a pure product, and the released NaOH is returned to the etch tank along with the dialysed NaOH. Dialysis allows recovery of essentially all of the NaOH and completely eliminates the need for disposal of the waste etchant. An industrial installation of base dialysis has been operating successfully in a chemical milling plant in California since 1991.

See Colour Plate 48.

Further Reading

Bailey DE (1993) Acid recycling system. US Patent 5 264 123.

Davis TA (1991) Recovery of sodium hydroxide and aluminium hydroxide from etching waste. US Patent 5 049 233.

Marshall RD and Storrow JA (1951) Dialysis of caustic soda solutions. *Industrial and Engineering Chemistry. Engineering and Process Development* 42: 2934–2943.

Saddington AW and Julien AP (1938) Dialysis of aqueous caustic solution. US Patent 2 138 357.

Shigekuni N and Motomura K (1979) Diffusion dialysis method. Japanese Patent 54 136 580.

Zender J (1946) Process and apparatus for dialyzing solutions. US Patent 2 411 238.

Donnan Dialysis

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Introduction

Donnan dialysis is a separation process that utilizes counterdiffusion of two or more ions through an ion-exchange membrane to achieve a separation. It can also be viewed as a continuous deionization process. For example, water softening can be done with a cation–exchange membrane. Hard water flows on one side of the membrane, and NaCl brine flows on the other side. Na^+ ions from the brine diffuse across the membrane and cause the Ca^{2+} and Mg^{2+} ions to diffuse in the opposite direction. Donnan dialysis is usually performed as a continuous, countercurrent process so that a substantial portion of a cation from a dilute solution could be concentrated into a small volume. Differences in the volumes and concentrations of the two solutions can be exploited to achieve some interesting and useful separations.

Donnan dialysis can be used for changing compositions of process or analytical solutions, pollution control, and even deionization of a process stream. The deionization process, called 'neutralization dialysis', combines Donnan dialysis through both cation-exchange and anion-exchange membranes in one apparatus with H^+ and OH^- ions exchanging for the cation and anion of a salt.

In the discussions that follow, the fundamental principles of Donnan dialysis will be presented, and some of its applications and capabilities will be described. The type of equipment and membrane arrangements appropriate for both Donnan dialysis and neutralization dialysis will be presented.

Background

The Donnan dialysis process is named after F. G. Donnan who in 1924 described the equilibrium that resulted when a semipermeable membrane separated two solutions of electrolytes. NaA on one side and KA on the other. The membrane he used was prepared by filling the pores of parchment paper with a gel of copper ferrocyanide, and he used ferrocyanide as the common anion A of the two salts. When the initial volumes and concentrations of the two salt solutions were the same, counterdiffusion of equal amounts of Na^+ and K^+ through the membrane led to an equilibrium condition where the two solutions had equal concentrations of NaA and KA. But when